

TRANSPORT OF OIL/WATER PARTITIONING COMPONENTS DURING WATER INJECTION

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Summary

The oil/water partitioning components such as alkylphenols and aliphatic acids naturally exist in crude oil compositions at different initial concentrations of hundreds or even thousands of ppm depending on the location of the reservoir compared to the site of original rocks. During contact with sweeping injection brine, those compounds diffuse from oil phase to water phase due to oil/water partitioning behaviours. As a result, their concentration in oil contacting with water will be attenuating during water injection. Their concentration profile in water injection history contains the information related to diffusion in oil and water phase, interstitial velocity of water and oil saturation.

This paper presents the research results of theoretical model and numerical model of the washed-out process of alkylphenols in the late stage of water injection. The research results have proposed approximate analytical expression for concentration of alkylphenols at the late stage of water flooding. In this regard, at the sufficient large injection volume the alkylphenol concentration attenuates exponentially and the attenuation rate depends on parameters such as partitioning coefficient, oil saturation and interstitial velocity of water and oil and diffusion coefficients. The simulation concentration results obtained from UTCHEM simulator for the 5-spot model showed a good match with analytical calculation results.

The research results can be used as the basis for developing methods to assess water flooding systems as well as oil saturation. The results can also be used for study of transport of non-aqueous phase liquid (NAPL) in environmental contamination.

Keywords: Residual oil saturation, waterflooding, tracer, partitioning organic compounds, enhanced oil recovery.

1. Introduction

Alkylphenols are aromatic compounds consisting of phenol nuclei and alkyl groups generated by alkylation and isomerisation reactions in the source rock during petroleum formation. For years, the existence and origin of the organic phenolic compounds such as alkylphenols and aliphatic acids in petroleum have been studied as indicators to classify petroleum according to the origin of hydrocarbons as well as to indicate petroleum migration pathways [1 - 4]. The concentration distribution of alkylphenols and their oil/water partition characteristics were used by Taylor, Larter, and Dale to study petroleum migration in the North Sea fields [4]. Lucach, Bowler, and Larter studied the Dhahaban hydrocarbon system in Oman based on the distribution variation of alkylphenols [5].

In the process where oil comes into contact with the injection water, because of oil/water partition properties the alkylphenols diffuse from oil phase to water phase, causing attenuation of their concentration in the two phases over time. The attenuation rate of alkylphenol concentration depends on several factors such as partition coefficient, diffusion coefficient, interstitial velocity of phases, and the amount of remaining oil in pore volume. Sinha, Asakawa, and Pope proposed a method using alkylphenols as natural tracers to determine residual oil saturation in the swept area based on their residence time in water phase during water injection [6].

In Vietnam, the Tracer Laboratory of the Centre for Applications of Nuclear Techniques in Industry (Vietnam Atomic Energy Institute) has studied the transport of alkylphenols during waterflooding in oil recovery since 2014. The authors have proposed an analytical model describing the attenuation of alkylphenol concentration in produced water over water injection time and conducted



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experiments to validate the analytical model [7 - 9]. The study results also considered the possibility of using alkylphenols as the natural partitioning tracers to evaluate oil saturation and determine the water contribution proportion of injection wells to production wells.

2. Theory

Alkylphenols (APs) are trace compositions in crude oil formed along with hydrocarbons during geochemical processes, which have the initial concentration in the oil phase in the range from several ppm to thousands of ppm depending on the field. During water injection, alkylphenols diffuse from oil phase to water phase at the water-oil contact boundary in pore spaces.

The advection-dispersion equation in oil-water phase contact of alkylphenols with the assumption that their concentration between phases instantaneously reaches equilibrium is expressed as Equation (1) [10]:

$$\phi \frac{\partial}{\partial t} (S_w C_w + K_d S_o C_w) + \nabla \cdot (S_w \phi \vec{v}_w^* C_w + K_d S_o \phi \vec{v}_o^* C_w) - \nabla \cdot [(S_w \phi \vec{D}_w^* + K_d S_o \phi \vec{D}_o^*) \nabla C_w] = 0 \tag{1}$$

in which, ϕ is porosity of media, C_w is APs concentration in water phase [M/L³]; S_w and S_o are the saturation of water phase and oil phase, respectively ($S_w + S_o = 1$); K_d is APs partition coefficient; \vec{v}_w^* and \vec{v}_o^* are interstitial velocity of water phase and oil phase, respectively [L/T]; \vec{D}_w^* and \vec{D}_o^* are dispersion tensors of APs in water phase and oil phase, respectively [L²/T], t is time [T].

Suppose that the porous media is infinite homogeneous, the saturation of the phases is constant, and the interstitial velocity of phases is constant in the pore, the initial and boundary conditions are as follows:

$$\text{Initial condition: } C_w(x, 0) = \begin{cases} C_o & x \in [0, +\infty) \\ 0 & x \in (-\infty, 0) \end{cases} \tag{2}$$

$$\text{Boundary condition: } C_w(-\infty, t) = 0 \tag{3}$$

$$\left. \frac{\partial C_w(x, t)}{\partial x} \right|_{x \rightarrow +\infty} = 0 \tag{4}$$

The one-dimensional analytical solution describing the concentration of APs in water phase $C_w(x, t)$ is described as:

$$C_w(x, t) = \frac{1}{2} \times C_o \times \left[1 + \text{Erf} \left(\frac{x - \frac{C^*}{A} \times t}{2 \times \sqrt{\frac{B \times t}{A}}} \right) \right] \tag{5}$$

in which, A, B and C* are parameters depending on APs partition coefficient, oil saturation, dispersion coefficient in phases, and pore velocity of water and oil:

$$\begin{aligned} A &= 1 + (K_d - 1)S_o \\ B &= (1 - S_o)D_{Lw}^* + K_d S_o D_{Lo}^* \\ C^* &= (1 - S_o)v_{wx}^* + K_d S_o v_{ox}^* \end{aligned}$$

At $x = L$ when $t \rightarrow \infty$, the approximate form of $\text{Ln}C_w$ is shown in Equation (6):

$$\text{Ln}[C_w(L, t \rightarrow \infty)] = -\frac{C^{*2}}{4 \times A \times B} \times t - \frac{1}{2} \times \text{Ln}(t) + \text{Ln} \left[\frac{A \times \sqrt{\frac{B}{A}} \times C_o \times \left(-1 + e^{\frac{C^* \times L}{2 \times B}} \right)}{2 \times C^* \times \sqrt{\pi}} \right] \tag{6}$$

Equation (6) shows that the value of $\text{Ln}(t)$ is very small compared to t , so it can be considered that $\text{Ln}C_w$ is approximately linear dependent on the time of water injection. Figure 1 illustrates $\text{Ln}C_w$ according to Equation (5) and the approximate solution according to Equation (6), representing the attenuation of APs concentration with different partition coefficients in water phase over injection time. When injection time t is sufficiently long or the injected volume is large enough, $\text{Ln}C_w$ is almost linear over injection time, in which the slope of $C^*2/$

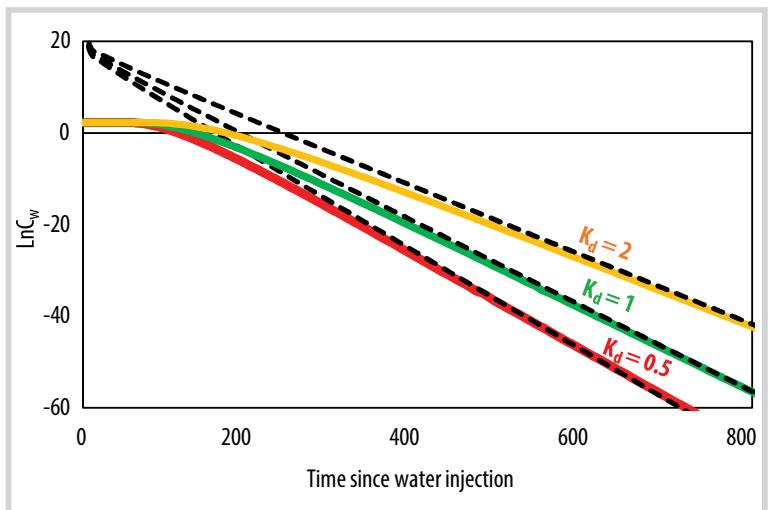


Figure 1. Illustrating $\text{Ln}C_w$ according to Equation (5) - solid lines and approximate solutions according to Equation (6) - dashed lines, for APs having $K_d = 0.5$, $K_d = 1$ and $K_d = 2$. When t is large, the value of $\text{Ln}C_w$ decreases linearly over time. The smaller the K_d , the faster the time to reach the linear asymptotic.

(4AB) represents the decline rate of APs concentration during water sweeping. With the same injection conditions and oil saturation, the smaller the K_d is, the greater the dispersibility into water phase becomes and the faster the concentration decreases, and vice versa.

The slope is described as

$$a = \frac{C^{*2}}{4 \times A \times B} = \frac{[(1 - S_o) \times v_{wx}^* + K_d S_o v_{ox}^*]^2}{4 \times [1 + (K_d - 1) \times S_o] \times [(1 - S_o) \times D_{Lw}^* + K_d \times S_o \times D_{Lo}^*]} \quad (7)$$

Let $a = a_i + a_m$, in which:

$$a_i = \frac{(1 - S_o)^2 \times v_{wx}^{*2}}{4 D_{Lo}^* S_o^2 \times K_d^2 + 4 (D_{Lo}^* + D_{Lw}^*) (1 - S_o) S_o K_d + 4 D_{Lw}^* (1 - S_o)^2} \quad (8)$$

$$a_m = \frac{2(1 - S_o) S_o v_{wx}^* v_{ox}^* K_d + S_o^2 v_{ox}^{*2} K_d^2}{4 D_{Lo}^* S_o^2 \times K_d^2 + 4 (D_{Lo}^* + D_{Lw}^*) (1 - S_o) S_o K_d + 4 D_{Lw}^* (1 - S_o)^2} \quad (9)$$

We have

$$\frac{a_m}{a_i} = \left(\frac{S_o}{1 - S_o} \right)^2 \times \left(\frac{v_{ox}^*}{v_{wx}^*} \right)^2 K_d^2 + 2 \times \frac{S_o}{1 - S_o} \times \frac{v_{ox}^*}{v_{wx}^*} \times K_d \quad (10)$$

and

$$\frac{v_{xo}^*}{v_{xw}^*} = \frac{1 - S_o}{S_o} \times \frac{f_o}{f_w} \quad (11)$$

in which, f_o and f_w are the oil cut and the water cut, respectively. Replace Equation (11) to Equation (10):

$$\frac{a_m}{a_i} = \left(\frac{f_o}{f_w} K_d \right)^2 + 2 \frac{f_o}{f_w} K_d \quad (12)$$

From the above equations, recall the decline rate of $\text{Ln}C_w$ ($L, t \rightarrow \infty$) be the leaching rate at the late stage of water flooding:

$$a = \frac{\left(1 + \frac{f_o}{f_w} K_d \right)^2 (1 - S_o)^2 v_{wx}^{*2}}{4 D_{Lo}^* S_o^2 K_d^2 + 4 (D_{Lo}^* + D_{Lw}^*) (1 - S_o) S_o K_d + 4 D_{Lw}^* (1 - S_o)^2} \quad (13)$$

At the late stage of water flooding, oil is almost immobile as also known as residual oil, $f_o = 0$ and $S_o = S_{or}$, the attenuation of APs concentration in the production water is in accordance with the exponential law of the injection time or respectively the injection volume. Obviously, the decline rate depends on the partition coefficient of APs (K_d), the oil saturation (S_o), the dispersion coefficients of APs in phases (D_{Lo}^*, D_{Lw}^*) and the pore velocity of water v_{wx}^* .

3. Simulation results

The advection-dispersion transport of APs from the oil phase into water phase during the water injection has been simulated on $\frac{1}{4}$ 5-spot models using UTCHEM (The University of Texas's Chemical Simulator software), developed by the University of Texas [11].

UTCHEM was used to run 3D homogeneous single-layered reservoir models with $\frac{1}{4}$ 5-spot pattern, including 2 specific cases:

- Immobile oil model having initial oil saturation and residual oil saturation of 0.35;
- Mobile oil model having initial oil saturation of 0.65 and residual oil saturation of 0.35.

The models have the size of 165 m \times 165 m \times 12 m divided into 55 \times 55 \times 4. The flow rate of injection water is 65.34 m³/d.

The general parameters of the models are:

- Porosity $\phi = 0.2$, water viscosity $\mu_w = 0.7$ cp, oil viscosity $\mu_o = 4$ cp;
- Longitudinal and transverse dispersivity are $\alpha_{DL} = 0.03$ m, $\alpha_{DT} = 0.003$ m;

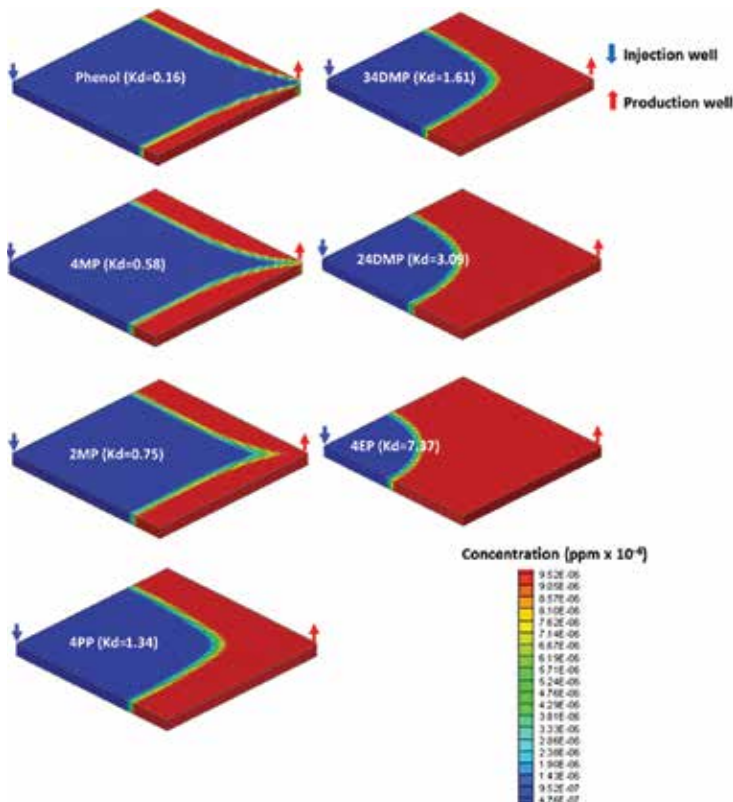


Figure 2. Illustration of APs concentration distribution in space at water injection of 0.6 PV in mobile oil model ($S_{oi} = 0.65, S_{or} = 0.35$).

Table 1. The partition coefficient K_d of APs and initial concentration of APs used in the models

Alkylphenols	Partitioning coefficient $K_d = C_o/C_w$	Initial concentration in oil phase (mg/L)	Initial concentration in water phase (mg/L)
Phenol	0.16	1.6	10
4-Methylphenol (4MP)	0.58	5.8	10
2-Methylphenol (2MP)	0.75	7.5	10
4-Propylphenol (4PP)	1.34	13.4	10
3,4-Dimethylphenol (34DMP)	1.61	16.1	10
2,4-Dimethylphenol (24DMP)	3.09	30.9	10
4-Ethylphenol (4EP)	7.37	73.7	10

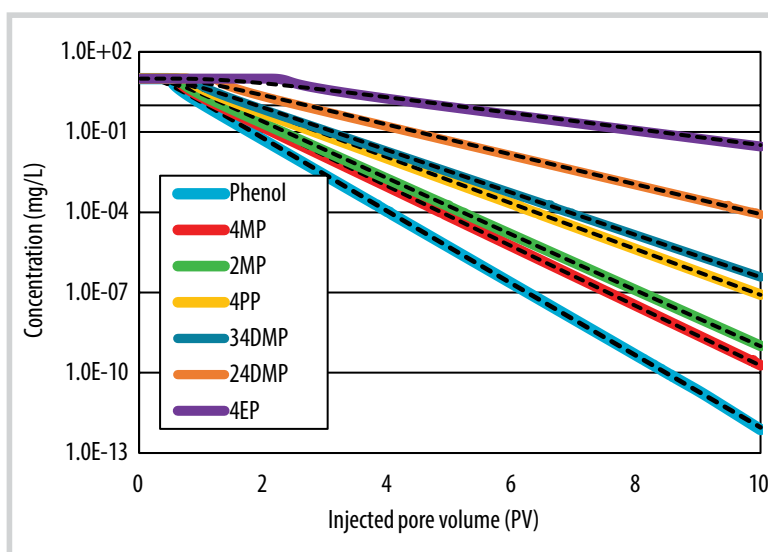
- Relative permeability curve is described by Corey model: critical water saturation $S_{cwr} = 0.3$, residual oil saturation $S_{or} = 0.35$, water endpoint: 0.15, oil endpoint 0.85, water exponent: 1.5, oil exponent: 2, endpoint mobility ratio: 1.

The APs initial concentration in oil phase and water phase and partition coefficient between phases determined in the experimental data of the Tracer Laboratory of CANTI are listed in Table 1. All compounds are supposed to have the same density, alkane number and chemical properties but different in partition coefficient.

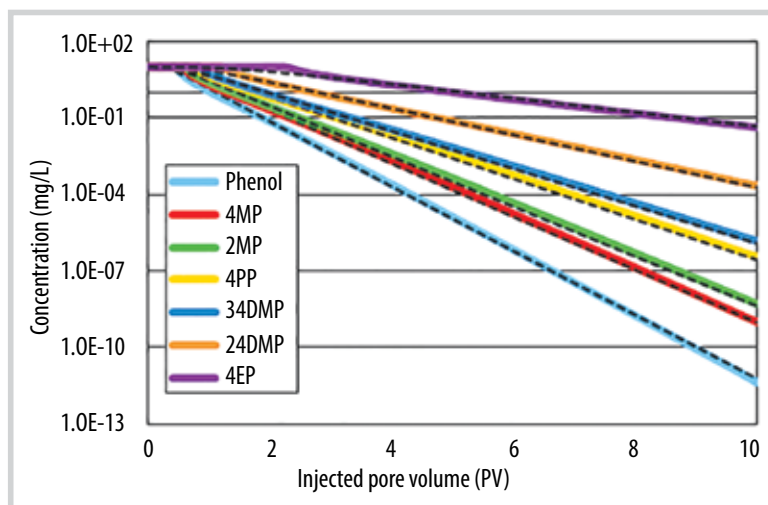
The water injection takes place up to 10 PV of the model to investigate the APs concentration decrease at the end of the injection stage. It is assumed that the concentration of APs between phases instantaneously reaches equilibrium while oil and water are in contact. Figure 2 illustrates the spatial concentration distribution of APs at water injection of 0.6 PV for the mobile oil model.

Figure 3 shows the concentration of APs in produced water in both models, in which the smaller the K_d is, the faster the leaching rate becomes, and vice versa.

The concentration obtained from calculation of the analytical solution in accordance with Equation (5) matches well with the simulation data in both models of mobile and immobile oil at the late stage of water injection (> 2 PV). The root mean square error (RMSE) between the simulation data and the calculation



(a)



(b)

Figure 3. Concentration curves of APs in produced water of the 1/4 5-spot having immobile oil ($S_{oi} = S_{or} = 0.35$, a) and the 1/4 5-spot having mobile oil ($S_{oi} = 0.65 S_{or} = 0.35$, b). Solid lines present the simulation data from UTCHEM software, while dashed lines present the calculation results of Equation (5).

tion data during the injection stage is shown in Table 2. The results show that the value of RMSE from 0 - 2 PV is greater than that at the

Table 2. The root mean square error (RMSE) between the simulation data and the analytical solution during the injection stage

Water injection (PV)	Phenol ($K_d = 0.16$)	4MP ($K_d = 0.58$)	2MP ($K_d = 0.75$)	4PP ($K_d = 1.34$)	34DMP ($K_d = 1.61$)	24DMP ($K_d = 3.09$)	4EP ($K_d = 7.37$)
	Immobile oil model						
0 - 1	1.445	1.585	1.638	1.813	1.883	1.174	0.123
1 - 2	0.080	0.130	0.150	0.170	0.220	1.930	1.950
2 - 3	0.003	0.010	0.015	0.044	0.064	0.183	2.382
3 - 4	< 0.001	< 0.001	< 0.001	0.005	0.009	0.062	0.177
4 - 5	< 0.001	< 0.001	< 0.001	< 0.001	0.001	0.015	0.197
5 - 10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	0.059
Mobile oil model							
0 - 1	1.115	1.377	1.469	1.744	1.849	1.285	0.215
1 - 2	0.118	0.161	0.169	0.147	0.169	1.939	2.103
2 - 3	0.001	0.004	0.006	0.018	0.029	0.109	2.469
3 - 4	< 0.001	0.002	0.003	0.007	0.007	0.025	0.118
4 - 5	< 0.001	< 0.001	< 0.001	0.002	0.003	0.004	0.144
5 - 10	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	0.002	0.046

end of the injection stage, in which the APs with higher K_d represents the higher RMSE value.

5. Conclusions

The analytical solution of the advection-dispersion equation describing the attenuation of concentration of APs compounds in produced water was approximated as an exponential function at the late stage of water flooding when the injection time or injected volume is large (>1 PV). The analytical solution was validated by applying the ¼ 5-spot model to calculate the concentration of 7 AP compounds to compare with the results of numerical simulation using UTCHEM simulator. The results show that, when the injection time is large enough to reach injection of 2 PV or more, the approximate analytical solution matches quite well with the simulation results. The RMSE value is less than 0.2 for the APs having K_d less than 3. The analytical solution also shows that the APs concentration in produced water decreases exponentially over injection time and the factors affect the concentration attenuation rate include partition coefficient, diffusion coefficients, interstitial velocity and oil saturation. The approximate solution obtained in this study provides a better understanding of the factors influencing the attenuation of the APs concentration than the semi-experimental formula proposed by Huseby et al [10].

The research results can be used as the basis for developing the methods of assessment of water flooding sys-

tem as well as oil saturation. The results can also be used for study of transport of non-aqueous phase liquid (NAPL) in environmental contamination.

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